Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

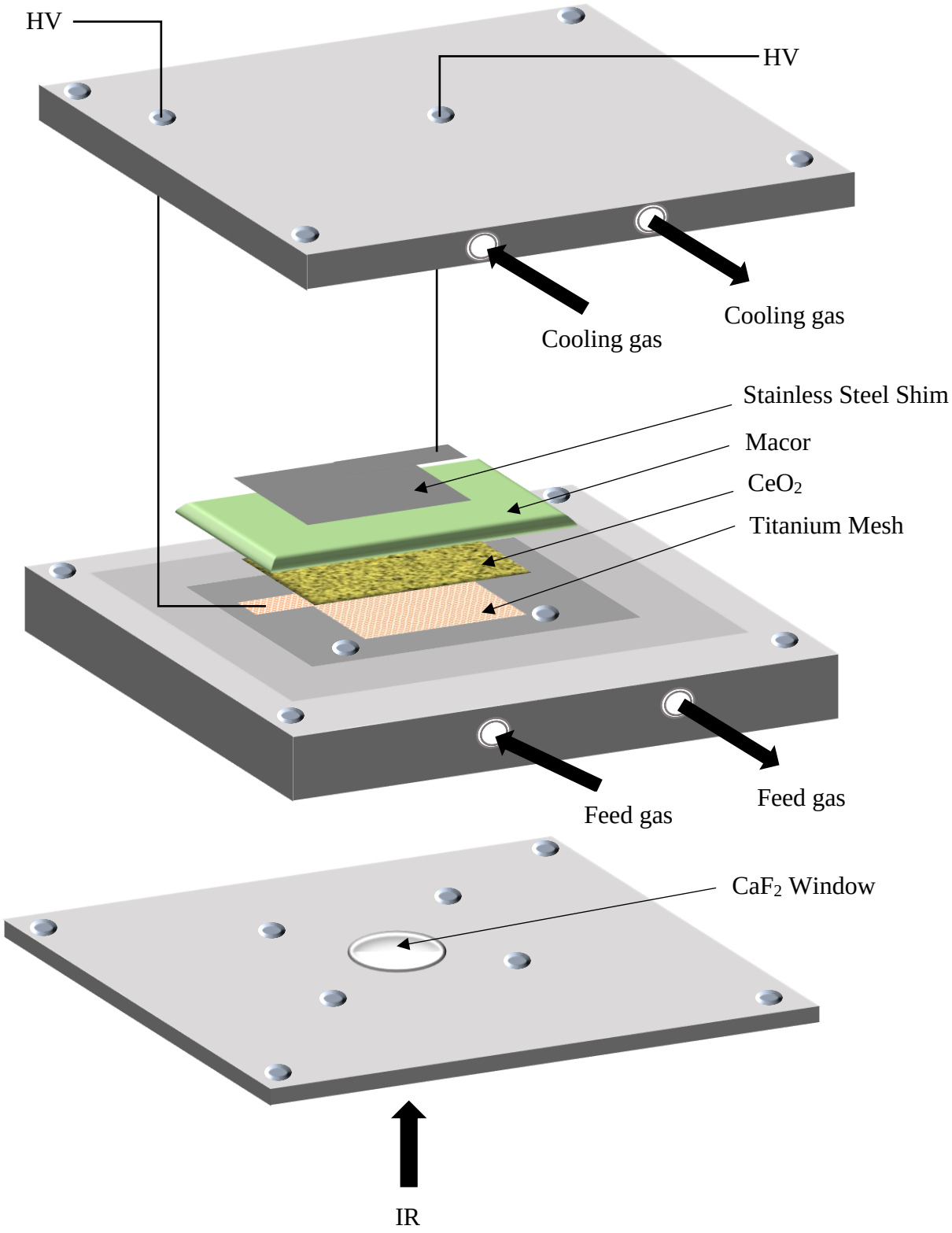
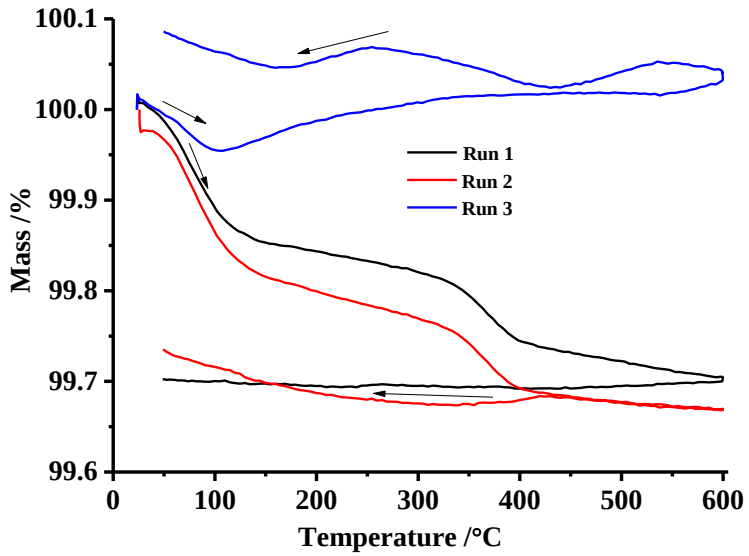
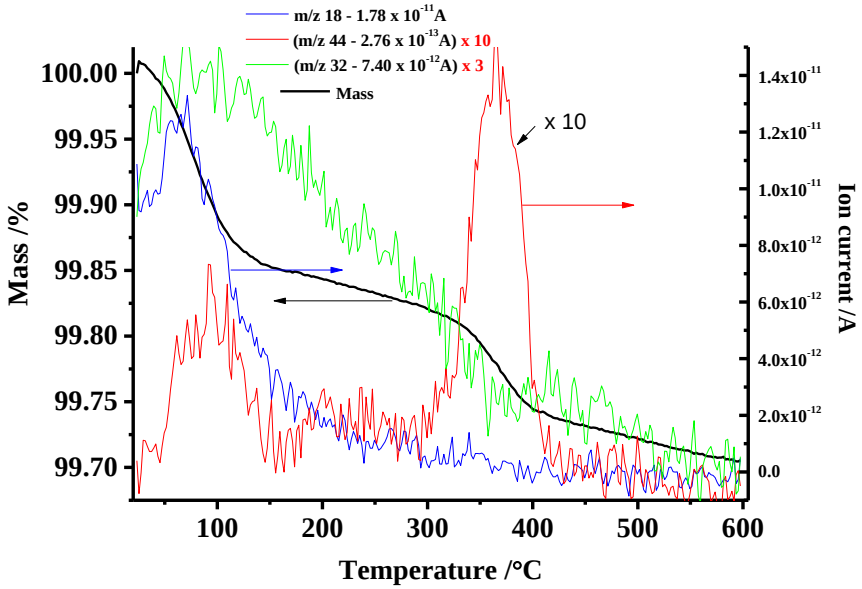


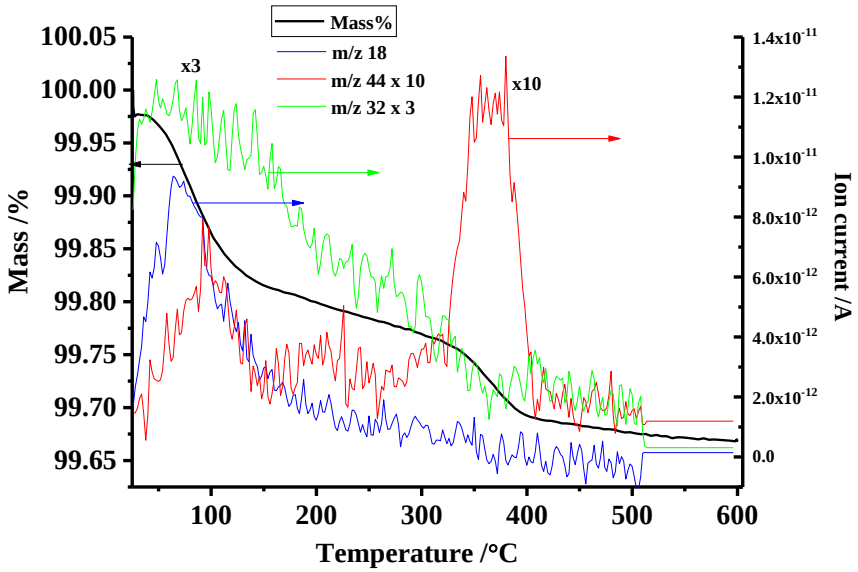
Figure S1. Schematic of the reflectance cell


Run 1
Run 2
Run 3
Mass /%
Temperature /°C

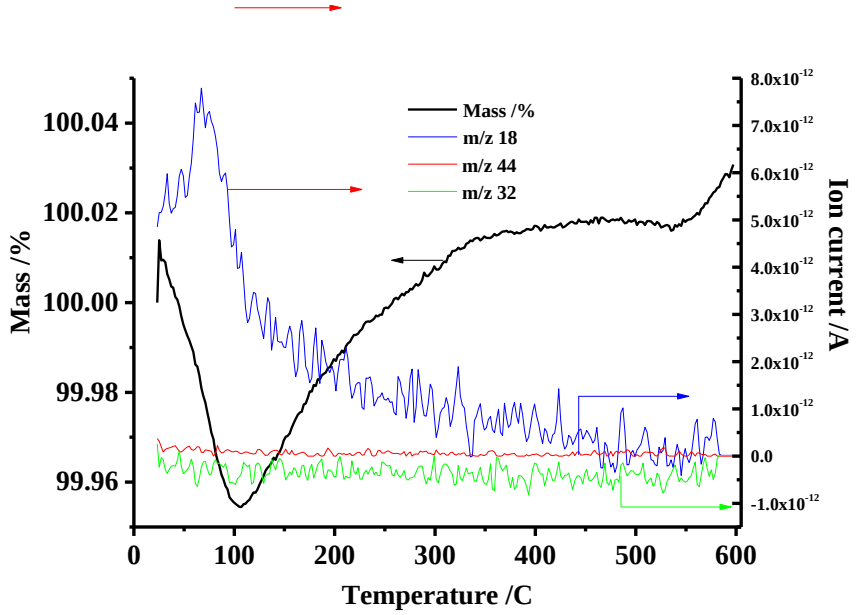
(a)


m/z 18 - 1.78 x 10-11A
(m/z 44 - 2.76 x 10-13A) x 10
(m/z 32 - 7.40 x 10-12A) x 3
Mass
x 10
Mass /%
Ion current /A
Temperature /°C

(b)



(c)



(d)

Figure S2. (a) The thermogravimetric response of 55.5 mg of CeO_2, heated in 40 cm^3 min^{-1} flowing N_2 at 5°C min^{-1} from room temperature to 600 °C (Run 1). The sample was held at 600 °C for 10 minutes and then cooled at 5°C min^{-1} to room temperature. (b) & (c) The m/z = 18, 32 and 44 responses recorded during the first and second heating cycles (Runs 1 and 2, respectively) of the sample in (a): the m/z = 32 responses are enhanced by a factor of 3 and the m/z = 44 responses by a factor of 10. (d) The m/z = 18, 32 and 44 responses recorded during the third heating of the sample in (a), Run 3. Run 1 was carried out on day 1 and the sample left in air overnight. Run 2 was carried out on day 2 and the sample left in flowing nitrogen overnight and run 3 carried out the following day.

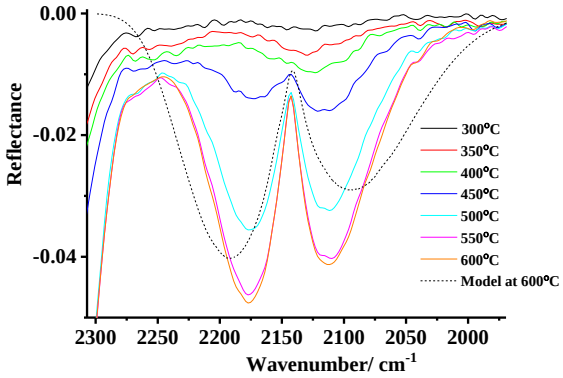
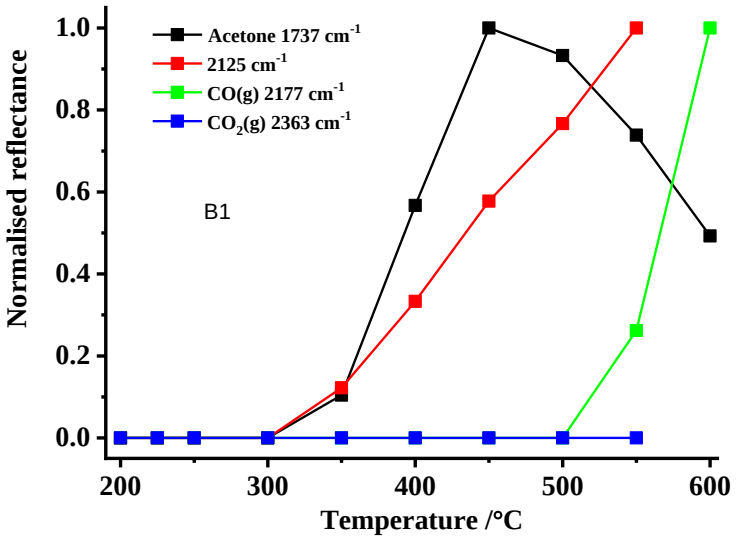
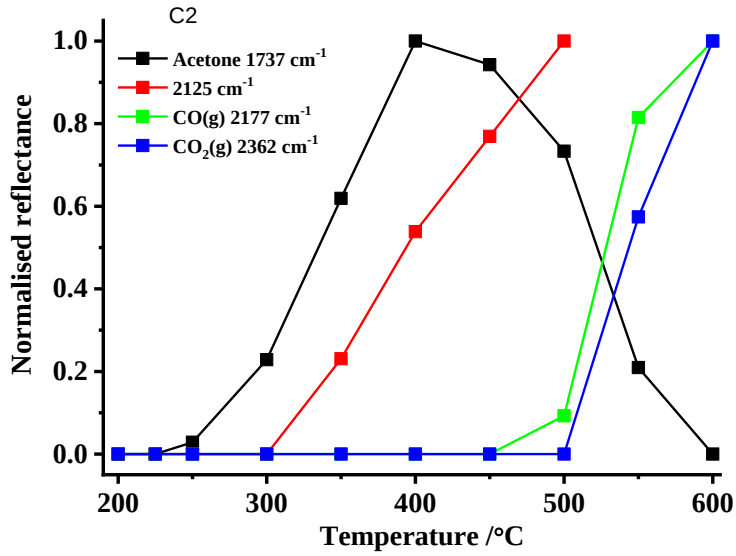


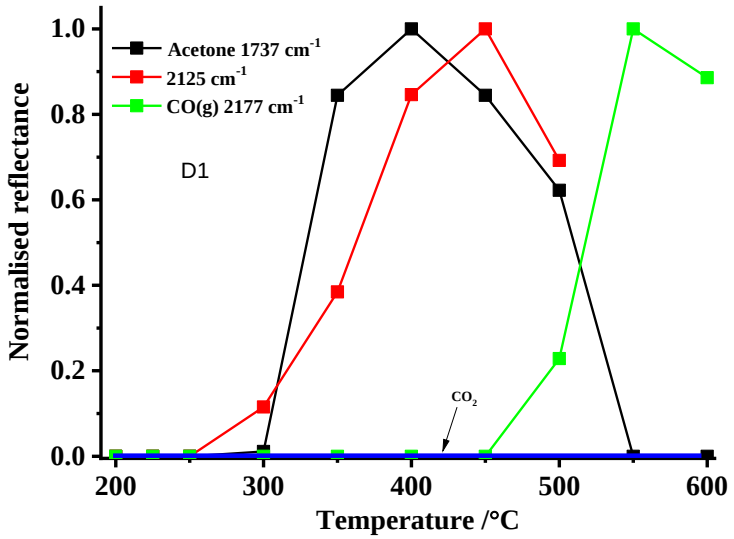
Figure S3. Spectra showing the CO spectral region collected at temperatures > 300°C from sample D2 during the experiment depicted in Figs. 3(a) – (d) with the spectrum collected at 300°C subtracted. Also shown is the spectrum of CO at 600˚C modelled using Spectralcalc, see text for details.


Acetone 1737 cm-1
2125 cm-1
CO(g) 2177 cm-1
CO2(g) 2363 cm-1
B1
Normalised reflectance
Temperature /°C
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
500
600

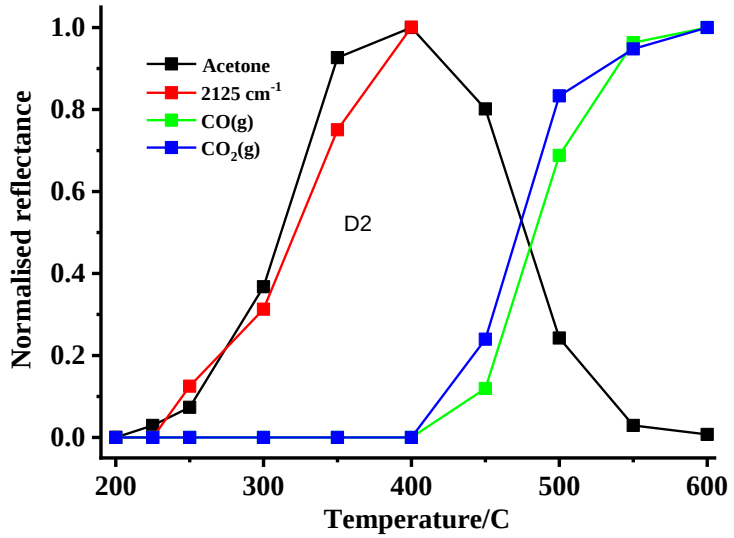
(a)


C2
Acetone 1737 cm-1
2125 cm-1
CO(g) 2177 cm-1
CO2(g) 2362 cm-1
Normalised reflectance
Temperature /°C
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
500
600

(b)

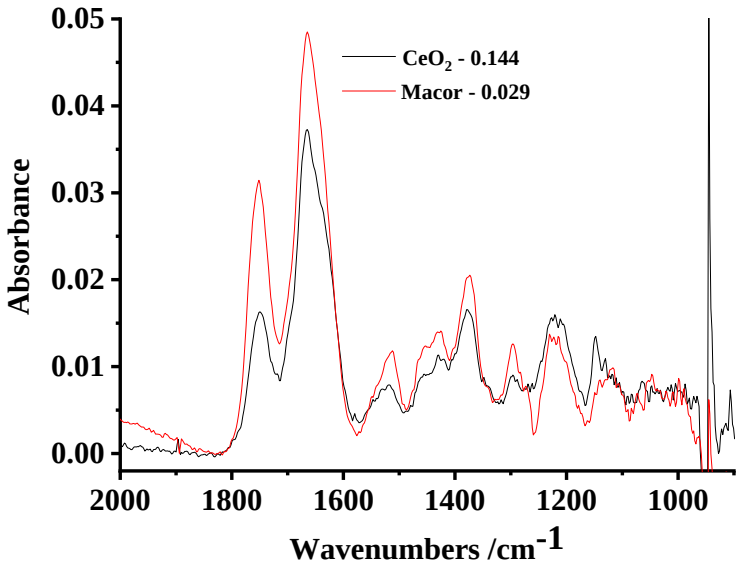


(c)

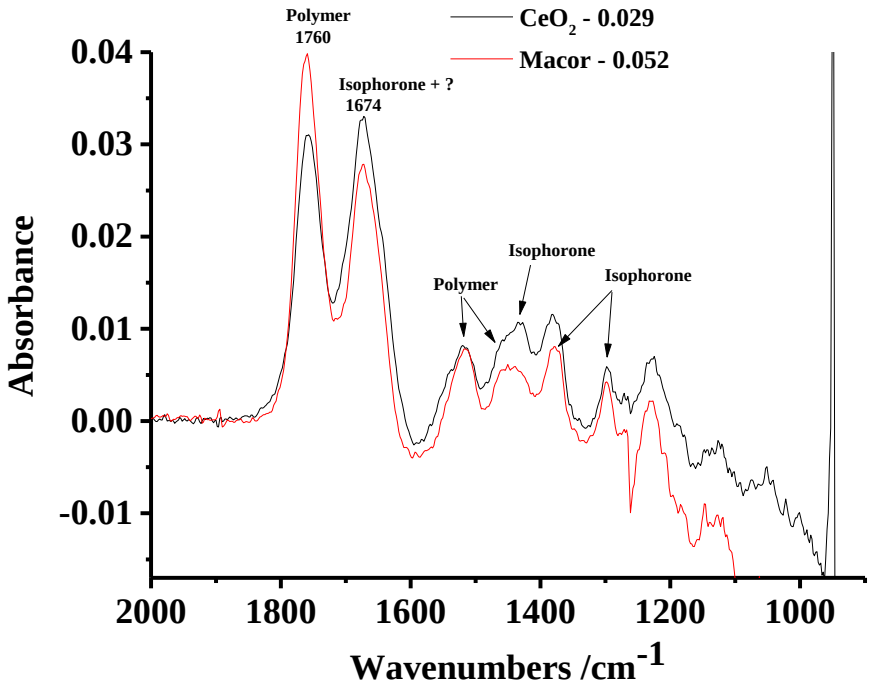


(d)

Figure S4. The plots in Figs. 4(a) – (d) normalised to their maximum values and plotted according to sample.



(a)



(b)

Figure S5. Spectra collected (a) after 8 minutes and (b) after 20 minutes during experiments carried out at 16W input power and using a nitrogen+IPA feed at a total flow rate of 30 cm^3 min^{-1} with CeO_2 or Macor as the dielectric in the plasma reflectance cell. In (a) the analogous spectra collected after 1 minute were subtracted, and in (b) the spectra collected after 8 minutes were subtracted. The spectra were offset down as indicated to facilitate comparison.

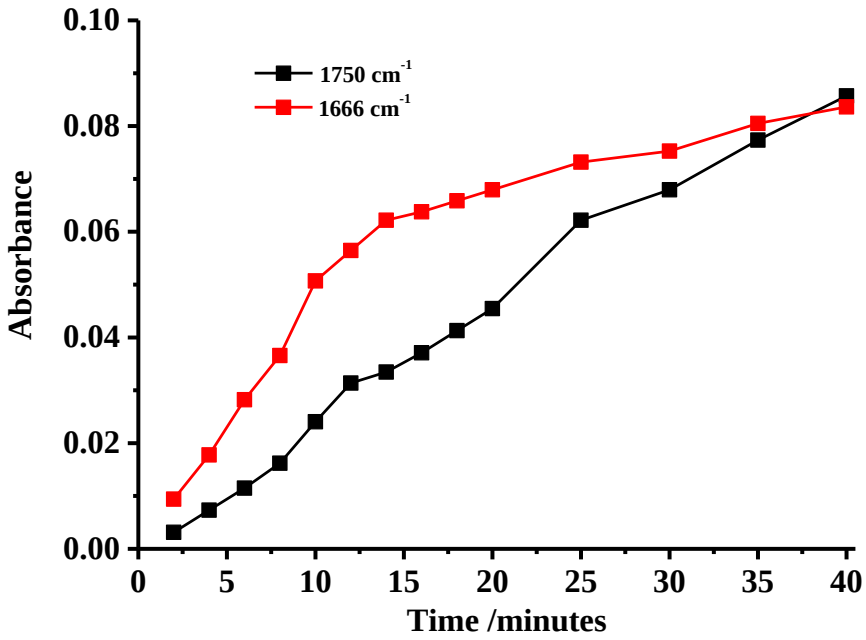


Figure S6. Plots of the 1750 and 1666 cm^{-1} bands in Fig. 5 as a function of time.